^{29}Si and ^{27}Al High-Resolution MAS-NMR Spectra of Phyllosilicates[1]

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Abstract: High-resolution ^{29}Si and ^{27}Al MAS-NMR spectra of polycrystalline 2:1 phyllosilicates have been recorded at 59.6 and 78.2 MHz, respectively. The spectra distinguish clearly between tetrahedral and octahedral coordination of aluminium, since the chemical shift of the Al signal for these coordinations is 60–70 and 0–10 ppm, respectively. Chemical shifts of ^{29}Si and ^{27}Al signals depend on the nature of second neighbor cations located in the tetrahedral and octahedral sheets and in the interlayer space. In the ^{29}Si spectra components associated with Si surrounded by three Si, two Si + Al, one Si + two Al, and three Al have been identified. From the relative intensities of these components it has been possible to determine tetrahedral Si/Al ratios and to show that Loewenstein's rule (avoidance of tetrahedral Al–O–Al linkages) is obeyed.

Introduction

The general features of phyllosilicate structures have been known for many years, but there are certain aspects concerning the distribution of ions in the different structural sites that have not been well established. Essentially, 2:1 phyllosilicates consist of layers made up by condensation of a central octahedral sheet and two tetrahedral sheets, one on each side. In the tetrahedral sheet, individual silica tetrahedra are linked with three neighboring tetrahedra to form hexagonal patterns in the layer plane. Octahedral compositions conform closely to either a full occupancy of the sheet if cations are M^{2+} (trioctahedral minerals) or an occupancy of two-thirds the available positions if cations are M^{3+} (dioctahedral minerals). Layers as described are electrically neutral, but in most cases, isomorphous substitutions in the tetrahedral sheet, essentially Al for Si, and/or the octahedral sheet confer to the layers a net negative charge that is compensated by interlayer cations. Location of the layer charge and, in general, distribution of isomorphous replacements are important crystallochemical characteristics that control the stability of the structure and the physicochemical behavior of these minerals. However, the determination of ion distribution by diffraction methods presents serious difficulties because isomorphous replacements do not necessarily follow a regular periodic pattern within the lattice.

NMR spectroscopy affords a valuable adjunct to diffraction methods in the analysis of ion distribution in crystalline solids. In particular, MAS-NMR spectroscopy permits one to distinguish between octahedral and tetrahedral coordination of Al[2] and to establish the different chemical environment of Si in aluminosilicate structures.[3]

In this paper we present the results of a systematic study of well-characterized phyllosilicates by MAS-NMR spectroscopy. Al in tetrahedral and octahedral sheets of phyllosilicates has been clearly identified. Appropriate selection of samples has allowed us to analyze the influence of the nature of second neighbor cations located in the three different structural sites (tetrahedral, octahedral, and interlayer) on the chemical shift of Si and Al nuclei. Moreover, the analysis of the relative intensities of the different components in the ^{29}Si spectra has permitted delineation of some of the factors that govern Si, Al distribution in the tetrahedral sheet of phyllosilicates.

Experimental Section

Samples. Samples of representative species among 2:1 phyllosilicates with compositions close to the ideal ones have been selected. These include members of the dioctahedral and trioctahedral series with various tetrahedral Si/Al ratios and with different interlayer compositions.

Structural formulas of the mineral species studied in this work are given in Table I. Samples have iron contents below 1.2%. A specimen of phlogopite with an iron content of 2.6% by weight has also been included in order to elucidate the influence of paramagnetic ions on NMR spectra.

NMR Spectroscopy. ^{29}Si and ^{27}Al MAS-NMR spectra of phyllosilicate samples in powder form were recorded on a Bruker CXP 300hp spectrometer at 59.6 and 78.2 MHz, respectively. The rotor used was of the conical Andrew type, and the spinning frequency was in the range 4–4.5 KHz. All measurements were carried out at room temperature with $Al(H_2O)_6^{3+}$ and tetramethylsilane used as external standards. Cross polarization and proton decoupling were not used. Time intervals between successive accumulations were chosen in order to avoid saturation effects and were 0.5 s for the ^{27}Al signal and 4 s for the ^{29}Si signal. Accumulation amounted to 50 and 500 FID's, respectively. The mean error in the measured isotropic chemical shifts was ~0.5 ppm.

Results and Discussion

^{27}Al Signal. ^{27}Al NMR spectra of samples of phyrophyllite, muscovite, and phlogopite are shown in Figure 1. The spectra consist of one or two principal components and a series of side bands associated to the spinning of the samples. According to previous work,[2] the central line at ~0 ppm must be assigned to octahedral Al ions and the line at ~70 ppm to tetrahedral Al ions. These assignments are in agreement with the structural compositions of these samples. Thus, pyrophyllite contains only Al_{oct}, while muscovite has both Al_{oct} and Al_{tet}. Although the ideal composition of phlogopite contains only Al_{tet} in our sample, there exists a small amount of Al for Mg substitution in the octahedral sheet that explains the small signal at ~0 ppm. In all cases, the Al_{tet} signal shows a greater half-width than the Al_{oct} signal.

In principle, a quantitative determination of Al_{tet}/Al_{oct} ratio seems to be possible considering the high resolution of the spectra. However, when we compared Al_{tet}/Al_{oct} ratios obtained from NMR spectra and from the mineralogical formulas, the agreement is poor. In the case of muscovite, the NMR spectrum overestimates the Al_{tet} content. The differences observed must be a consequence of second-order quadrupolar effects whose elimination in both signals would require higher magnetic fields than that used in this work (70 k G).

^{29}Si Signal. ^{29}Si MAS-NMR spectra of the different species of phyllosilicates are given in Figures 2 and 3. Talc and pyrophyllite have only Si in the tetrahedral sheet, and consequently all silicon ions have the same tetrahedral environment, i.e., Si surrounded by three Si. The NMR spectra of these samples show a single component that appears at −97 ppm for talc and at −94 ppm for pyrophyllite. The difference in chemical shift between these samples, as will be discussed later, is a consequence of differences in composition of the octahedral sheet. Lippmaa et al.[4] found also a single component for talc at −98 ppm, but in pyrophyllite they observed two components at −91.5 and −95 ppm

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[1] The results of this paper were presented at the 5th European Clay Meeting, Prague, Aug 1983, and at the US-Western Europe Seminar on Metal Complex Catalysts in Intracrystalline Environments, Brugge, Oct 1983.

[2] Müller, D.; Gessner, W; Behrens, H. J.; Scheler, G. *Chem. Phys. Lett.* **1981**, *79*, 59–62.

[3] Fyfe, C. A.; Thomas, J. M.; Klinowski, J.; Gobbi, G. C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 259–275.

[4] Lippmaa, E.; Mägi, M.; Samoson, A.; Engelhardt, G.; Grimmer, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 4889–4893.

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Table I. Structural Formulas of Phyllosilicate Samples[a]

	tetrahedral		octahedral							interlayer			
mineral species	Si	Al	Al	Ti	Fe^{3+}	Mg	Fe^{2+}	Li	Σ_{oct}	K	Na	Ca	Σ_{int}
pyrophyllite[b]	4.00		1.92		0.04	0.07			2.03				
muscovite[c]	3.16	0.84	1.95		0.03	0.04			2.20	0.79	0.04	0.01	0.84
margarite[d]	2.11	1.89	1.99			0.03	0.01		2.03	0.01	0.19	0.81	1.01
talc[e]	4.00					2.98	0.02		3.00				
phlogopite P8[f]	2.84	1.16	0.09	0.06		2.82	0.02		2.99	0.87	0.06	0.03	0.96
phlogopite P18[f]	2.96	1.04	0.01	0.02	0.03	2.71	0.17	0.03	2.97	0.95	0.04	0.03	1.02
vermiculite[g]	2.89	1.11	0.08	0.02	0.06	2.82			2.98	0.03		0.46[h]	0.49

[a] All values refer to an $O_{10}(OH)_2$ formula unit. [b] North Carolina. Orcel, J.; Caillere, S.; Henin, S. *C. R. Hebd. Seances Acad. Sci.* **1957**, *244*, 1383–1386. [c] Miyori, Tochigi, Japan. Kodama, H.; Gatineau, L.; Mering, J. *Clays Clay Miner.* **1971**, *19*, 405–413. [d] Chester, MS. Guggenheim, S.; Bailey, S. W. *Am. Mineral.* **1975**, *60*, 1023–1029. [e] Tijola, Spain. Alvarez-Estrada, D. "Talcos espanoles"; Monografia, CSIC: Madrid, 1952. [f] Greenville and Wakefield, Quebec, Canada. Rousseaux, J. M.; Rouxhet, P. G.; Vielvoye, L. A.; Herbillon, A. *Clay Miner.* **1973**, *10*, 1–16. [g] Llano, County, TX. Norrish, K. *Proc. Int. Clay Conf., 1972*, **1973**, 417–432. [h] The natural vermiculite contains Mg^{2+} as exchangeable cations, but, for convenience, chemical analysis was done in a calcium-exchanged sample.

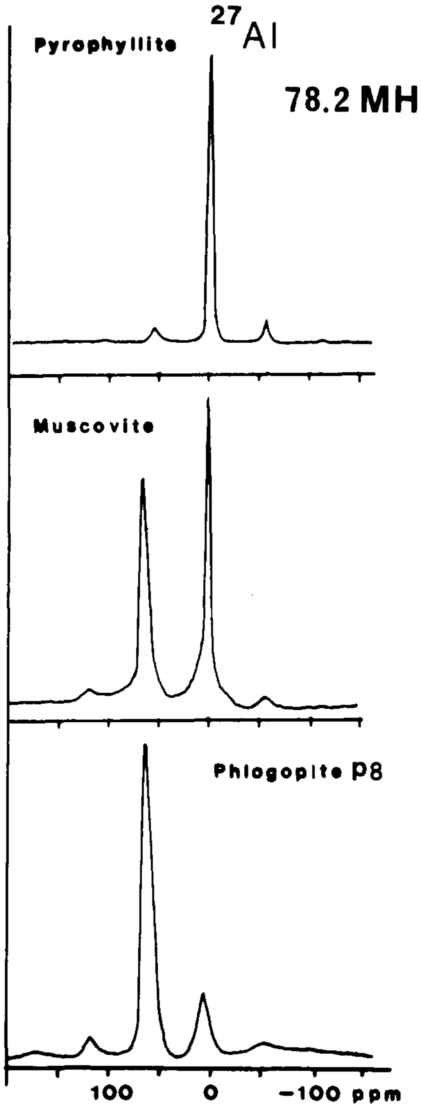

Figure 1. ^{27}Al MAS-NMR spectra of pyrophyllite, muscovite, and phlogopite recorded at 78.2 MHz, showing the lines corresponding to tetrahedral and octahedral Al. Chemical shifts are given from $Al(H_2O)_6^{3+}$.

that they attributed to differences in chemical octahedral environment of Si. It must be remembered, however, that in pyrophyllite all the tetrahedral Si have the same second neighbors in the octahedral sheet and consequently only one line should be expected. Probably the splitting observed by Lippmaa et al.[4] is due to the presence of other mineralogical phases in their sample.

In the micas phlogopite and muscovite, approximately one-fourth of the Si in the tetrahedral sheet is replaced by Al. These substitutions confer a net negative charge to the layers that in both cases is compensated by interlayer K ions located between the hexagonal rings of oxygens of two adjacent layers. For each composition, all silicon atoms of the tetrahedral sheet have the same second neighbors in both the interlayer space and the octahedral sheet. Therefore, differences of environments for Si can be only a consequence of the Al, Si distribution. There exist four possible distinct environments for Si within the tetrahedral sheet of micas, i.e., SiO_4 surrounded by three SiO_4, two SiO_4 + one AlO_4, one SiO_4 + two AlO_4, and three AlO_4. By analogy to the case of zeolites,[5] they will give signals with less negative values

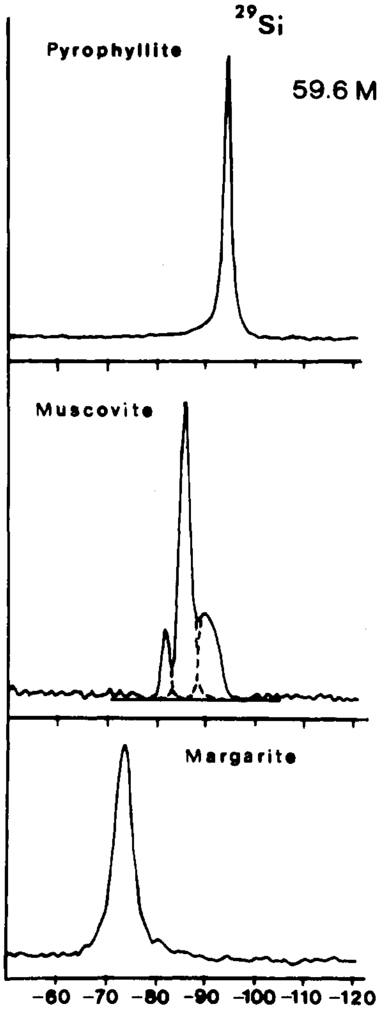

Figure 2. ^{29}Si MAS-NMR spectra of the dioctahedral phyllosilicates pyrophyllite, muscovite, and margarite, recorded at 59.6 MHz. Chemical shifts are given from Me_4Si.

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(5) Klinowski, J.; Ramdas, S.; Thomas, J. M.; Fyfe, C. A.; Hartman, J. S. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1025–1050.

Table II. ^{29}Si and ^{27}Al Isotropic Chemical Shifts in Phyllosilicates[a]

	Si signal				Al signal	
mineral species	Si(Si$_3$)	Si(Si$_2$Al)	Si(SiAl$_2$)	Si(Al$_3$)	Al$_{tet}$	Al$_{oct}$
pyrophyllite	−94					+1
muscovite	−89	−85	−81		+67	+1.5
margarite				−73	+71	+2
talc	−97					
phlogopite P8	−91	−86	−82		+63.5	+6
vermiculite	−92	−88	−83.5		+62.5	+5

[a] Values are given in ppm from Me_4Si and $Al(H_2O)_6{}^{3+}$, respectively.

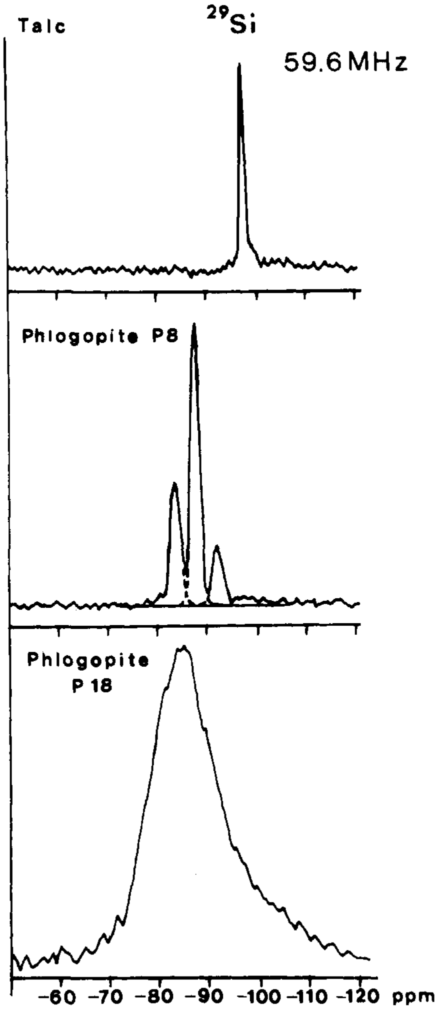

Figure 3. ^{29}Si MAS-NMR spectra of the trioctahedral phyllosilicates talc and phlogopite, recorded at 59.6 MHz. Phlogopite P18 contains 2.6% by weight of iron. Chemical shifts are given from Me_4Si.

for the chemical shift as the Al content increases. The ^{29}Si MAS-NMR spectra of these micas show three well-resolved components at −91, −86, and −82 ppm for phlogopite and −89, −85, and −81 ppm for muscovite. Considering that in these micas Si/Al ratios are near 3, the three AlO_4 environment should have a very low probability and consequently the observed lines should be assigned to Si surrounded by three Si, two Si + one Al, and one Si + two Al, respectively. This assignment agrees with the structural formulas of the two samples. Thus, in the phlogopite sample with its higher tetrahedral Al content ($Si_{2.84}Al_{1.16}$) than that in muscovite ($Si_{3.16}Al_{0.84}$), the signal corresponding to one Si + two Al environment has higher relative intensity than in the muscovite spectrum, while the signal corresponding to three Si environment follows the reverse trend.

In vermiculite with the same ideal composition as phlogopite but in which interlayer potassium has been substituted by hydrated Mg ions, the spectrum shows also three lines that appear at −92, −88, and −83.5 ppm. The relative intensities of the three lines are similar to those of phlogopites as one might expect from the composition of the tetrahedral sheet of vermiculite ($Si_{2.89}Al_{1.11}$) which is close to that of phlogopite.

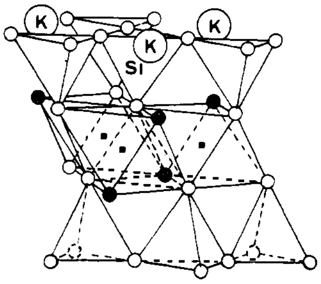

Figure 4. Details of the structure of 2:1 phyllosilicates showing second neighbors of the tetrahedral cations: ○, oxygen atoms; ●, OH ions; ■, octahedral cations.

Margarite with a Si/Al near 1 shows a single line at −73 ppm (Figure 2c), indicating the existence of only one kind of environment for the Si atoms. These results are in agreement with those obtained by Guggenheim and Bailey[6] from X-ray diffraction data, which show that margarite has a perfect long-range Si, Al ordering in space group *Cc*. With this distribution, Al and Si atoms alternate in the occupancy of tetrahedral sites and, therefore, each Si is surrounded by three Al and vice versa each Al is surrounded by three Si. Consequently the line observed at −73 ppm in the NMR spectrum should be assigned to the three Al environment.

In samples containing iron in the octahedral sheet, the lines are considerably broadened by paramagnetic interactions and the fine structure of the NMR spectra is lost. This effect is illustrated in the spectrum of phlogopite P18 that has a similar composition to that of phlogopite P8, except for the higher iron content (2.62% of Fe by weight). Thus, the applicability of the NMR method is limited to samples with low content of paramagnetic centers (below 1.5%).

Influence of Second Neighbor Cations on the Position of ^{29}Si and ^{27}Al Signals. In 2:1 phyllosilicates, each tetrahedron shares corners with three neighboring tetrahedra while the fourth corner (apical oxygen) is shared with three octahedra. In micas, each tetrahedral ion has in addition three interlayer cations (K^+ or Ca^{2+}) as second neighbors that are positioned on the three contiguous hexagonal rings (Figure 4). On the other hand, each octahedron shares edges with six adjacent octahedra and also shares oxygens with four tetrahedra, two on each side of the octahedral sheet. The effect that those second neighbor cations located in different sites of the structure, tetrahedral sheet, octahedral sheet, and interlayer space, exert on the chemical shift of the Si and Al signals can be analyzed separately by comparison of pairs of samples with appropriate compositions. The positions of Al and Si signals for the samples analyzed in this work are given in Table II and Figure 5.

The influence of the nature of tetrahedral cations on the Si and Al$_{tet}$ line positions has already been mentioned in the case of phlogopite and muscovite. The several Si lines observed in the mica spectra reflect the different tetrahedral environments of this cation. The position of these signals shifts by equal increments toward less negative values as the number of Al around Si increases. On the contrary, the spectra show only one Al$_{tet}$ signal,

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[6] Guggenheim, S.; Bailey, S. W. *Am. Mineral.* **1977**, *62*, 1158–1167.

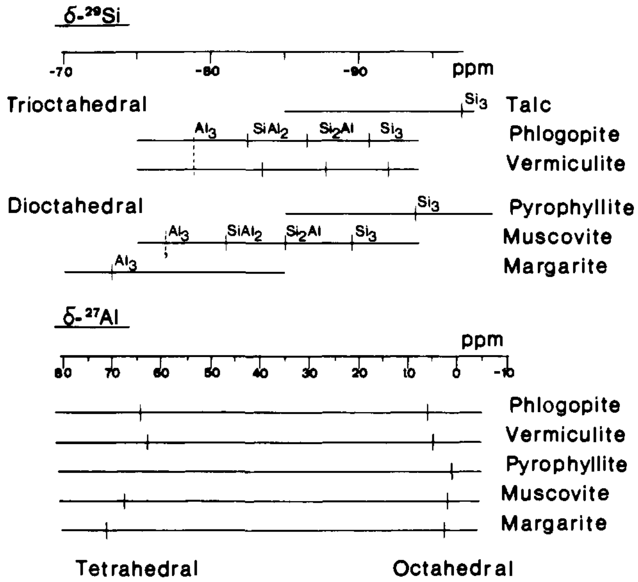

Figure 5. Comparison of chemical shifts of ^{29}Si and ^{27}Al for the different mineral samples. Assignments of the lines to different environments of Si and Al are indicated.

indicating that this cation has always the same tetrahedral environment.

The second factor that influences the position of the tetrahedral Si and Al signals is the composition of the octahedral sheet. When we compared samples having the same tetrahedral and interlayer compositions (talc–pyrophyllite, phlogopite–muscovite), it is observed that the positions of equivalent tetrahedral Si and Al lines shift toward higher values when passing from trioctahedral (three Mg) to dioctahedral (two Al and one vacancy) samples. An alternative explanation of the differences between trioctahedral and dioctahedral minerals could be the different position that protons occupy in these two compositions. It is well-known[7] that in trioctahedral minerals, OH bond axes are perpendicular to the layers and point toward the hexagonal cavities, while they are almost parallel to the layers in dioctahedral minerals. However, we think that the effect of the nature of octahedral cations, which are directly coordinated to the apical oxygens of the tetrahedra, should prevail.

The effect of the nature of interlayer cations on the line position is ascertained by comparison of the Si signal corresponding to the three Si environment in samples with the same octahedral composition. In the pairs talc–phlogopite and pyrophyllite–muscovite the presence of K^+ as second neighbors shifts that line to more positive values. A similar shift is observed when interlayer potassium is substituted by Ca^{2+} (margarite). For this mica, a single line is observed a −73 ppm that corresponds to Si surrounded by three Al. This value is more positive that the value one will expect for the same environment in muscovite, assuming a constant shift for each Al incorporated into the Si environment. The same tendency is observed for the signal of Al_{tet} when passing from muscovite (67 ppm) to margarite (71 ppm).

With respect to the Al_{oct} signal, it is observed that its position is almost independent of the nature of interlayer cations, which are too far to exert a significant influence, and also of the composition of the tetrahedral sheet. Thus, in the dioctahedral phyllosilicates, pyrophyllite, muscovite, and margarite, Al_{oct} lines appear at about the same value (1–2 ppm). On the contrary, the composition of the octahedral sheet modifies slightly the position of the Al_{oct} signal. In trioctahedral minerals that contain small amounts of Al in the octahedral sheet (phlogopite and vermiculite), each Al ion must be surrounded by six Mg ions and the Al_{oct} line appears at 5–6 ppm, a value which is higher than those observed for dioctahedral minerals where each Al ion is surrounded by three Al and three vacancies.

In summary, our results show that the line position of tetrahedral Si and Al depend on the nature of the cations located as second neighbors of these nuclei in the tetrahedral sheet, the octahedral sheet, and the interlayer space. In the case of Al_{oct} the position of the NMR line seems to depend only on the nature of cations located as second neighbors in the octahedral sheet.

Si, Al Ordering Schemes in Micas. Structural analysis by X-ray diffraction methods and MAS-NMR spectra demonstrate that margarite with a Si/Al ratio near 1 has a perfect long-range Si, Al ordering.[6] Si and Al ions alternate in the occupancy of tetrahedral sites, and therefore Loewenstein's rule that forbids Al ions to occupy contiguous tetrahedra is obeyed.

In the case of muscovite and phlogopite with Si/Al ratios near 3, detailed structural studies do not give any proof for a long-range tetrahedral cation order.[8] The presence of a short-range order is difficult to detect by diffraction methods, but in favorable cases, it can be ascertained by spectroscopic methods. From the analysis of ^{29}Si MAS-NMR spectra it is possible to elucidate certain aspects of Si, Al distribution and in particular to check the validity of Loewenstein's rule.[5] If we assume that no Al–O–Al linkages are present in those micas, it is possible to calculate Si/Al ratios from the ^{29}Si NMR spectra according to the expression

$$(\mathrm{Si/Al})_{\mathrm{NMR}} = \sum_{n=0}^{3} I_{\mathrm{Si}(n\mathrm{Al})} \Big/ \sum_{n=0}^{3} (n/3) I_{\mathrm{Si}(n\mathrm{Al})}$$

where $I_{Si(nAl)}$ is the integrated intensity of the nth component in the NMR spectrum, n being the number of Al ions surrounding a particular Si tetrahedron (in our case 0, 1, 2, or 3). The good agreement between Si/Al ratio values calculated from the mineralogical formulas (3.7 for muscovite and 2.5 phlogopite) and by ^{29}Si NMR spectra (3.6 for muscovite and 2.7 for phlogopite) clearly demonstrates that Loewenstein's rule is obeyed in micas. This is also true for vermiculite, the mineral formed by alteration of a parent trioctahedral mica; in this case, the Si/Al ratio from both the structural formula and the NMR spectrum is 2.6.

When one compares experimental and model-generated ^{29}Si NMR spectra, assuming a random distribution of Si and Al, it is shown that the restriction of Loewenstein's rule improves appreciably the fitting between experimental and calculated intensities. However, there are still significant differences, indicating the existence of other factors besides Loewenstein's rule that govern Si, Al distribution in the tetrahedral sheet of micas. Different models of distribution are being assayed actually in order to eludicate the nature of those factors. The results will be the subject of a forthcoming paper.

Concluding Remarks

High-resolution MAS-NMR spectroscopy affords a valuable adjunct to diffraction methods in crystal structure analysis of aluminosilicates. It permits one to distinguish between tetrahedrally and octahedrally coordinated aluminum and also the different chemical environments of tetrahedrally coordinated silicon. From these results, it is possible to elucidate local ordering schemes in the distribution of isomorphous replacements (Si, Al), which is difficult to be established by X-ray diffraction methods. Moreover, this method offers a potential use in monitoring reactions taking place in ceramic processes and in determining the conditions at which minerals were formed in nature.

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Registry No. ^{29}Si, 14304-87-1; Al, 7429-90-5; pyrophyllite, 12269-78-2; muscovite, 1318-94-1; margarite, 1318-86-1; talc, 14807-96-6; phlogopite, 61076-94-6; vermiculite, 1318-00-9.

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(7) Serratosa, J. M.; Bradley, W. F. *J. Phys. Chem.* **1958**, *62*, 1164–1167.

(8) Bailey, S. W. In: "Crystal Structures of Clay Minerals and their X-ray Identification"; Brindley, G. W., Brown, G., Eds.; Mineralogical Society: London, 1980; pp 2–123.